SwRI 08-2457

CHARACTERIZATION OF SNOWMOBILE PARTICULATE EMISSIONS

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FINAL LETTER REPORT

Prepared for

Yellowstone Park Foundation, Inc.
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June 1999

June 29, 1999

TO: Yellowstone Park Foundation, Inc.
37 East Main Street, Suite 4
Bozeman, MT 59715

ATTN: Ms. Kezha Hatier-Riess
Program Director

SUBJECT: Final Letter Report, "Characterization of Snowmobile Particulate Emissions," SwRI Project 08-2478.

I. INTRODUCTION

The project effort covered in this final report was conducted by Southwest Research Institute for the Yellowstone Park Foundation under a consulting contract. Funding was provided primarily by the Pew Charitable Trusts, with additional funding from the National Park Service. Work was conducted following the outline provided in SwRI Revised Proposal Number 08-21615. The SwRI Project Number was 08-2457, and the SwRI project leader was James N. Carroll.

This study measured emissions from a Polaris snowmobile engine. Emission testing was conducted by SwRI s Department of Emissions Research in Nonroad Engine Test Cell 13. Basic criteria pollutants were measured, along with specialized analysis techniques to characterize particulate matter. The primary goal of this project was to characterize particulate emissions from a snowmobile engine through measurement of particulate matter volatile organic fraction (VOF), particle size, and biological activity. While it was originally proposed to use a MOUDI (micro-orifice uniform deposit impactor) system to characterize particle size, an improved technique called SMPS (scanning mobility particle sizer) became available, which provides more detailed information than MOUDI. SMPS was used to determine particle size information reported in this study.

Because fuel and lubricant are combusted together in conventional two-stroke engines, lubricants contribute to engine emissions. An aerosol of uncombusted lubricant is the primary source of two-stroke engine particulate emissions, as measured gravimetrically from diluted exhaust gas. Baseline particulate characterization was performed using both a mineral-based conventional two-stroke lubricant, and a bio-synthetic lubricant, to evaluate whether lubricant selection had a strong effect on particulate character.

II. ENGINE, FUEL AND LUBRICANTS

A. Engine Description

The engine used in this study was a Fuji Heavy Industries Model EC50PM06 snowmobile engine, described in Table 1, which is used in a variety of Polaris snowmobiles. The engine is considered representative of the snowmobile population in the Yellowstone area. The engine is carbureted, and employs oil injection provided by a crankshaft-driven pump, at a rate that is a function of engine speed and throttle position.

TABLE 1. DESCRIPTION OF TEST ENGINE

Snowmobile Manufacturer	Polaris
Engine Manufacturer	Fuji Heavy Industries
Engine Model	EC50PM06
Engine Serial Number	9702719
Operating Cycle	2-stroke
Displacement, cc	488
Cylinders	2
Cooling	Fan Air
Carburetion	2-Mikuni VM34SS
Main Jet Size	210
Ignition System	CDI
Spark Plug	BPR8ES
Lubrication	Oil injection

B. Fuel and Lubricants

Fuel flow was measured on a mass basis using a Micromotion coriolis-effect liquid flow meter, and was also calculated from dilute emissions using a carbon-balance method. The fuel used during this study conforms to federal light-duty vehicle emissions certification gasoline specifications. Table 2 contains the analyses of this fuel, which has SwRI designation EM-2392-F. The lubricants used were Polaris s mineral-based two-stroke oil for baseline emissions testing, and Conoco s bio-synthetic two-stroke oil. The lubricant analyses are shown in Table 3.

TABLE 2. TEST FUEL PROPERTIES

SUPPLIER HOWELL HYDROCARBONS

LOT NO. 96C-12 SwRI CODE EM-2392-F

Item	CFR Specification [a]		Supplier Analysis	SwRI Analyses
	ASTM	Unleaded		
Octane, research	D2699	93 (min.)	97.5	97.9
Sensitivity		7.5 (min.)	7.9	8.4
Pb (organic), g/U.S., gal	D3237	0.05 [b]	<0.005	0.001
Distillation Range:				
IBPEF	D86	75-95	89	104
10% Point, EF	D86	120-135	129	137
50% Point, EF	D86	200-230	225	227
90% Point, EF	D86	300-325	320	323
EP, EF	D86	415 (max.)	403	398
Sulfur, wt. %	D1266	0.10 (max.)	.008	.001
Phosphorus, g/U.S.,gal	D3231	0.005 (max.)	<0.0008	0.0009
RVP, psi	D323	8.7-9.2	9.15	8.77
Hydrocarbon Composition:				
Aromatics, %	D1319	35 (max.)	31.1	28.8
Olefins, %	D1319	10 (max.)	1.2	0.4
Saturates	D1319	c	67.7	70.8

[a] Gasoline fuel specification as in CFR 86.113-94(a)(1) for light-duty gasoline vehicles.

[b] Maximum

[c] Remainder

TABLE 3. LABORATORY ANALYSIS OF LUBRICANTS

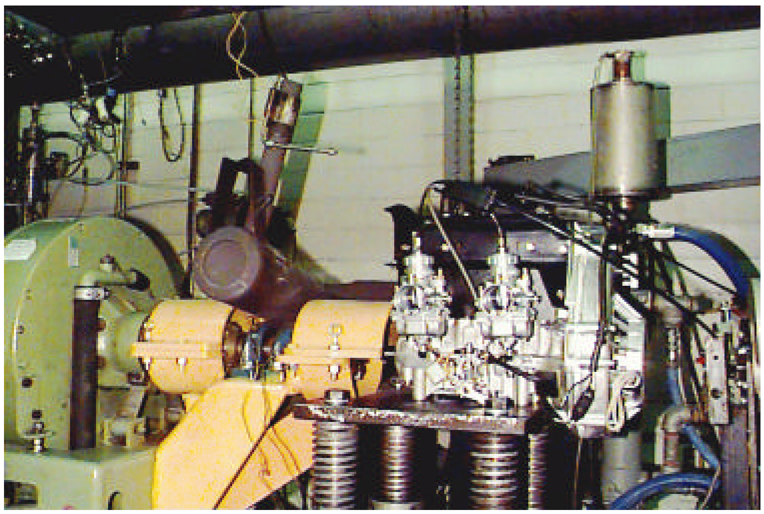
Property	Method	POLARIS 2S	CONOCO Biosynthetic
Specific Gravity	ASTM D-4052	0.8691	0.9265
Viscosity @ 40EC, cSt	ASTM D-445	36.28	55.62
Viscosity @ 100EC, cSt	ASTM D-445	6.63	9.05
Flash Point, EC	ASTM D-92	100	244
Total Base Number	ASTM D-4739	6.24	1.18
Total Acid Number	ASTM D-664	0.50	0.68
Carbon, wt. % Hydrogen, wt. %	ASTM D-5291	84.32 13.73	75.52 12.13
Nitrogen, wt. %	ASTM D-5291	0.591	0.245
Ba, ppm Ca, ppm Mg, ppm Mn, ppm Na, ppm P, ppm Zn, ppm		<1 2 1 <1 <5 1 2	1 2 <1 <1 3 186 1
Distillation by GC, EC IBP 5% 10% 20% 50% 80% 90% 95% FBP	ASTM D-2887	 178 185 190 200 478 525 545 562 607	 318 400 469 484 492 605 618 692 728

III. TEST FACILITIES AND METHODOLOGY

A. Test Facilities

The snowmobile engine was tested in SwRI s nonroad engine test cell. The engine was mounted on a bed plate using jack stands, and connected to a Schenck Model W130 175Hp eddy-current dynamometer using an appropriate coupling. Figure 1 shows the Polaris test engine.

The engine was operated using its stock intake air box and exhaust system to ensure correct operation.



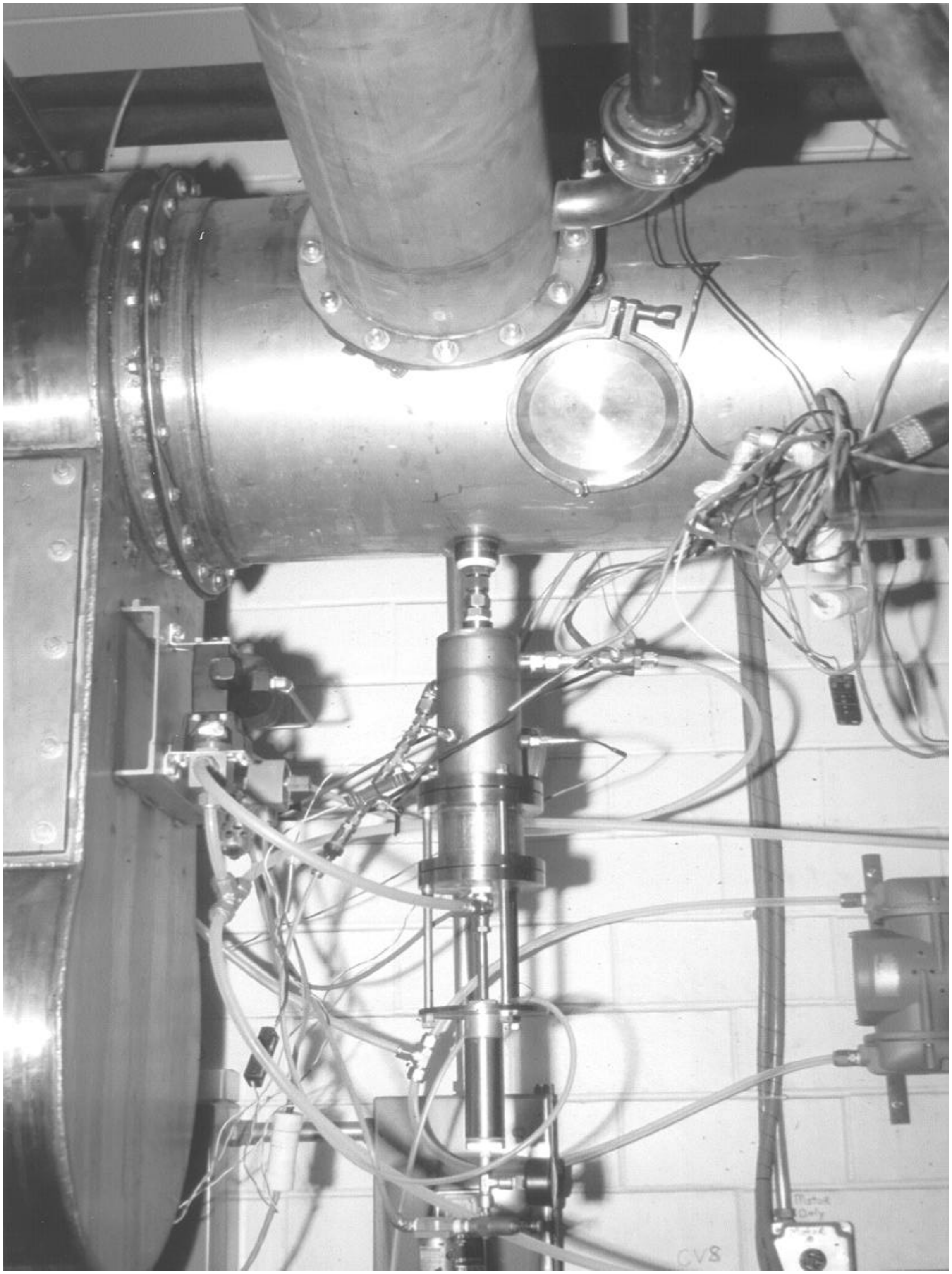
All engine exhaust was collected without physical connection to the exhaust system, and conveyed to a 0.457 m (18 in) diameter dilution tunnel. Total dilute flow was maintained at approximately 26.5 scmm (1000 scfm). Proportional bag samples of diluted exhaust were collected for THC, CO, NO_x, and CO_2 analysis. A portion of the diluted exhaust stream was further diluted in a secondary dilution tunnel for particulate measurement, as shown in Figure 2.

B. Basic Emissions Sampling and Analysis Methods

Emissions were measured using a 5-mode steady-state snowmobile engine test cycle that was developed for the International Snowmobile Manufacturers Association by SwRI. This cycle is described in Table 4.

TABLE 4. SNOWMOBILE ENGINE TEST CYCLE

Mode	1	2	3	4	5
Speed, %	100	85	75	65	Idle
Torque, %	100	51	33	19	0
Wt. Factor, %	12	27	25	31	5



Modes are run in order from highest to lowest speed. One hundred percent engine speed is the speed declared by the snowmobile manufacturer as representative of the maximum steady engine speed in snowmobile operation. Torque values are specified as a percent of the maximum (WOT) torque observed at 100 percent speed in Mode 1.

Total hydrocarbons (THC), carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM), and carbon dioxide (CO_2) were measured from diluted exhaust in every test. Instrumentation used included a heated flame ionization detector (HFID) for THC, non-dispersive infrared analyzers for CO and CO_2, and a chemiluminescent analyzer for NO_x. Particulate was measured using 90-mm Pallflex filtration of double-diluted exhaust gas following 40 CFR Part 86, Subpart N protocols.

C. Particulate Characterization

1. Direct Filter Injection - Gas Chromatography (DFI/GC)

The portion of diluted engine exhaust that is collected on a Teflon coated glass fiber filter at temperatures below 125EF is, by CFR definition, particulate matter (PM). Two-stroke engine PM has been described as being composed primarily of unburned lubricant, along with carbon, unburned fuel, and other components. Several techniques are available to distinguish volatile organics from soot and other compounds. For this study, DFI/GC analysis was used to help characterize PM emissions from the two-stroke spark-ignited snowmobile engine.

The analysis for the volatile organic fraction (VOF) of particulate was carried out by first collecting particulate material on Teflon-coated glass fiber filters, and then analyzing these samples using a Perkin-Elmer Model 8500 Gas Chromatograph (GC), equipped with a uniquely designed filter injection system, and a flame ionization detector (FID).

For DFI/GC analysis, a 10 percent pie-shaped slice of the particulate filter is cut and folded so that no particulate material is exposed. Next, the filter slice is placed into the injector, and the injector is placed into the cool zone of the DFI/GC inlet to allow any oxygen in the system to be purged without the loss of any sample. When all air has been purged from the system with clean nitrogen, the injector is inserted into the hot zone of the DFI/GC inlet where all volatile material is desorbed and deposited onto the 40°C column. A GC oven temperature program is then run to separate the desorbed compounds by boiling point. As a standard, the same analysis is performed on a filter slice on which a weighed amount of engine test oil has been deposited. The response in the FID (area counts) is ratioed to the known mass of engine test oil. To calculate the lubricating oil contribution, these boiling point separations (or distributions) of the PM are analyzed mathematically by superimposing the chromatogram of the VOF of the test engine oil onto the chromatogram of the VOF of the PM sample.

2. Scanning Mobility Particle Sizer

A TSI Scanning Mobility Particle Sizer (SMPS) was used to provide information on particulate number concentration and size distributions in the range from 8 nm to 300 nm. This instrument works on the principle of particle electric mobility. It consists of a neutralizer, a mobility section, a TSI Model 3025A condensation particle counter (CPC), and a computerized control and data acquisition system, as shown in Figure 3.

Particles in the sample stream first pass through a Krypton bipolar ion charger/neutralizer. This brings the particle charge distribution to a well defined level. The aerosol then enters the annular mobility section close to the inner surface of the outer cylinder. Clean sheath air flows close to the central rod. When a voltage scan is applied to the rod, charged particles move in the radial direction inward or outward, depending on their polarity. Particles with the right polarity and electrical mobility exit through holes at the bottom of the central rod. These particles are then detected by the CPC.

In order to utilize the SMPS, which is very sensitive to low levels of PM and can become contaminated by high particle concentrations, a partial dilution system was constructed which could provide very high dilution ratios. A schematic of the partial dilution system is shown in Figure 4. It consists of two identical dilution stages. The primary dilution stage consists of an air ejector pump that draws a sample of raw exhaust, and mixes it with clean air. The second dilution stage is mounted in series downstream of the primary sampling zone section. Dilution ratios produced by the ejector pumps were measured using the ratio of CO concentration in the exhaust, over the diluted CO concentrations at the primary and secondary stages during sampling operations.

3. Bioassay Analysis

Bioassays are defined here as short-term tests that measure damage to genetic material (DNA). This damage (referred to as genotoxicity), is thought to be an important mechanism in the process of developing cancer. The genotoxicity of the extracts from particulate matter serves as an index of DNA damage and provides some relative potency of the genotoxic compounds present on the particulate matter. The most widely used and validated bioassay for genotoxicity is the Salmonella/microsome test, or Ames test. The assay has been used for the screening of potentially carcinogenic compounds in the environment and has been used as a chemical "detector" for genotoxic compounds. Modifications of the assay have also been developed for specific applications.

Bioassay analyses of all samples was conducted by Dr. N. Kado and his group at the University of California, Davis, who use a modification of the Salmonella/microsome - Ames test called the microsuspension procedure. The modified assay is approximately 10 times more sensitive than the original Ames Salmonella assay, and allowed testing for low (microgram) levels of particulate matter. The material tested was an organic solvent extract of collected particulate matter from each mode of operation of the snowmobile engine. Mutagenic activity is presented on both a mass basis (revertants/μg PM), as well as revertants/hp-hr.

IV. TEST RESULTS

A. Criteria Pollutants

The Polaris engine was emissions tested using the 5-mode ISMA snowmobile engine test cycle. Criteria pollutants measured included HC, CO, NO_x, and particulate matter (PM). Two 5-mode tests were performed using two lubricants: Polaris s own mineral-based two-stroke oil (BASE), and Conoco s bio-synthetic two-stroke oil (BIO). A summary of the test results is shown in Table 5. Detailed test results are included in Appendix A.

TABLE 5. POLARIS SNOWMOBILE ENGINE EMISSIONS TEST SUMMARY

Test ID	Lubricant	Modal Emissions, g/hr				Engine Speed, rpm	Engine Power, hp
		HC	CO	NO_x	PM		
BASE Mode 1	Polaris	3516	14210	59.0	9.30	7000	51.4
BASE Mode 2	Polaris	2389	10973	9.2	11.10	5950	23.2
BASE Mode 3	Polaris	2160	5855	5.2	14.60	5250	13.4
BASE Mode 4	Polaris	1286	1591	4.2	14.40	4550	6.5
BASE Mode 5	Polaris	806	516	0.3	4.10	1600	-
Weighted BASE Total, g/hp-hr	Polaris	115.5	375.6	0.69	0.70		17.7 [a]
BIO Mode 1	Conoco	3658	14499	59.3	12.10	7000	51.7
BIO Mode 2	Conoco	2283	10801	10.5	18.30	5950	23.3
BIO Mode 3	Conoco	2200	5985	5.2	28.80	5250	12.9
BIO Mode 4	Conoco	1575	2525	3.4	35.20	4550	6.5
BIO Mode 5	Conoco	784	510	0.3	4.00	1600	-
Weighted BIO Total, g/hp-hr	Conoco	119.9	391.2	0.69	1.39		17.8 [a]
BIO/BASE		**104%**	**104%**	**100%**	**198%**		
[a] Weighted modal power							

Table 3 shows both modal emission rates and weighted total emissions rates. HC, CO, and PM are high, and NO_X emissions are low, as is typical of two-stroke engines. Particulate emission rates are more comparable to those of older, pre-control diesel engines. Measured emissions from this engine agreed well with data generated on a same-model Polaris engine in a recently completed project for the Montana Department of Environmental Quality.[1]

[1] J.J. White, J.N. Carroll, "Emissions from Snowmobile Engines Using Bio-Based Fuels and Lubricants," October 1998.

Gaseous emission rates from the two lubricants tested were very similar, at most differing by only 4 percent. However, the Conoco bio-synthetic lubricant produced nearly twice the particulate as the Polaris mineral-based lubricant. Again, previous testing in the above referenced project had shown similar increases in PM emissions using the Conoco lubricant.

It was noted that PM increased as engine speed and load decreased. This is likely due to poorer part load combustion, and the additional time available for particulate formation at lower engine flows. Particulate formation is a function of particle concentration, i.e., number of particles in a given volume, and the amount of time available for small particles to form from coagulation, and larger particles to form through deposition of volatile species and/or agglomeration by impact.

B. Particulate Matter Volatile Organic Fractions

The particulate-laden filters from each modal test were analyzed by DFI/GC to calculate volatile organic fraction (VOF), and the contribution of the lubricant to VOF. The remainder of PM is non-volatile and is generically termed soot. Table 6 shows a summary of the VOF results. Further details of the DFI/GC results are included in Appendix B.

TABLE 6. PARTICULATE DFI/GC ANALYSIS SUMMARY

Test ID	Lubricant	PM, g/hr	VOF, %	Volatile Organics, g/hr	VOF Fraction Unburned Oil, %
BASE Mode 1	Polaris	9.3	46	4.3	14
BASE Mode 2	Polaris	11.1	75	8.3	53
BASE Mode 3	Polaris	14.6	78	11.4	79
BASE Mode 4	Polaris	14.4	77	11.2	89
BASE Mode 5	Polaris	4.1	81	3.3	78
Weighted BASE Average		12.4	73	9.2	67
BIO Mode 1	Conoco	12.1	40	4.8	30
BIO Mode 2	Conoco	18.3	60	11.0	23
BIO Mode 3	Conoco	28.8	56	16.1	64
BIO Mode 4	Conoco	35.2	51	18.0	71
BIO Mode 5	Conoco	4.0	43	1.7	51
Weighted BIO Average		24.7	53	13.2	50
Avg. BIO / Avg. BASE		199%	72%	143%	75%

Two-stroke engines use a fuel and oil mixture to both produce power and lubricate the engine. As much as 30 percent of the intake charge passes through the engine uncombusted and exhausts to the atmosphere. As a consequence, the volatile particulate fraction was expected to be very high. Results shown in Table 6 confirm expectations. Weighted average volatile fraction of PM for the Polaris lubricant was 73 percent, and for the Conoco lubricant was 53 percent. These results may be affected by the species present, and may be understating the level of volatiles. Further work should be done with other techniques such as extraction and oven baking. Modern on-road diesel engines, which are designed for low particulate emissions, typically have particulate volatile fractions of 25 to 40 percent, including moisture and sulfates.

The weighted average unburned lubricant contribution to VOF was 67 percent and 50 percent for the Polaris and Conoco lubricants, respectively, which confirms the lubricant is the primary source of two-stroke engine PM. Note that although the bio-synthetic lubricant tests had less VOF and less unburned oil on a percentage basis than the mineral-based lubricant, the average VOF emission rate using the bio-synthetic lubricant was higher.

C. Particle Size Analysis

Particle size analysis was conducted using a Scanning Mobility Particle Sizer (SMPS), manufactured by TSI. Samples of raw exhaust were drawn into the specially designed sampling system shown in Figure 4, for dilution to levels appropriate for the SMPS. Duplicate analyses were performed during each test mode.

Particles initially form in the less than 50 nanometer range (nanoparticles) and then coagulate to become larger particles by colliding with each other. Coagulation is a function of both particle concentration and time. Thus, coagulation produces larger particles and reduces particle number and concentration over time. The range of particle sizes formed is called the distribution of the particles. The SMPS system scans a programmed range (8 - 300 nm) of particle sizes to measure their distribution and counts the particles during the scan. Particle sizes are logarithmically distributed, so the data collected was then split into logarithmically even particle size bins for graphical analysis.

Results of the two particle sizing tests performed in Mode 1 with the Polaris lubricant (BASE Mode 1) were analyzed to calculate total particle count, and find the mean of the size distribution. These are summarized in Table 7. Data given are the averages of the two tests performed in each engine mode. Tests run with the Polaris lubricant are prefixed with the name BASE, and tests with the Conoco lubricant are prefixed with the name BIO. Graphical results from all tests are included in Appendix C.

TABLE 7. PARTICLE SIZE SUMMARY

Test ID	Lubricant	Speed, rpm	Power, hp	Mean diameter, nm (10^{-9}m)	Concentration, particles/cc
Base Mode 1	Polaris	7000	51.7	23	13,394,194
Base Mode 2	Polaris	5950	23.3	24	43,370,481
Base Mode 3	Polaris	5250	12.9	35	480,257,409
Base Mode 4	Polaris	4550	6.5	51	349,044,854
Base Mode 5	Polaris	1600	0	81	20,255,643
Bio Mode 1	Conoco	7000	51.4	25	13,877,949
Bio Mode 2	Conoco	5950	23.2	26	488,317,493
Bio Mode 3	Conoco	5250	13.4	42	662,684,979
Bio Mode 4	Conoco	4550	6.5	72	243,247,136
Bio Mode 5	Conoco	1600	0	84	10,084,638

Results from these two tests are also shown graphically in Figures 5 and 6. Particle diameter is presented using a log-normal scale. These show a particle size distribution that is primarily in the less than 100 nanometer range (ultrafine regime). This is significant because particles in the ultrafine regime are respirable, and due to Brownian motion can easily be deposited in the lungs. In addition, both figures show a bi-modal distribution with two peaks. The peak at smaller diameter is in the nanoparticle range and may not be representative of 'real world' particulate. If the sample drawn into the SMPS sampling system had been from a previously diluted sample, the initial peak of nanoparticles could have had time to coagulate into larger particles. Further experimentation would be necessary to understand this bi-modality.

Figures 7 and 8 show the size distribution from the Mode 1 test with Conoco s bio-synthetic lubricant (BIO Mode 1). These do not show a bi-modal distribution. Whether the lack of bi-modality is due to the lubricant, or other factors, is unknown. However, from Table 5 we see that the mean diameter and concentration of the particles in Mode 1 are very similar to those with the Polaris lubricant. Table 5 also shows that the mean diameter in each mode is similar for both lubricants.

It was observed that as engine speed and load decrease, the mean particle diameter increases. This could be the result of additional time for coagulation at lower engine flowrates. However, most of the particles remain in the ultrafine regime. In addition, particle concentrations were highest at the medium speed and load Mode 3. These higher partic le concentrations are likely due to higher scavenging losses, and poorer combustion quality, which are typical of part-load two-stroke operation.

Another observation from the sizing data is that as load and speed decreased, the distribution became more regular. Figures 9 and 10 show the repeat tests from BIO Mode 2. These distributions are very regular in shape, and the figures for Modes 3, 4, and 5 in Appendix C also show more regular distributions. This may be due to the lower engine speeds, allowing more time for coagulation.

The SMPS data provides insight into the makeup of the particulate from snowmobile engines. One might have expected larger particle diameters from two-stroke spark-ignited engines, because the lubrication systems produce large droplets in the engine intake system. This, however, was not the case. In addition, the distribution of particle sizes in the ultrafine range showed a wide distribution of sizes, including large concentrations of particles in the nanoparticle range. These size distributions are similar to diesel particulate. Typically, diesel engines produce their highest particle concentrations in the 40 to 60 nm range. These data show that a large number of particles are produced by snowmobile engines, in this same range.

D. Particulate Bioassay

NOTE: Bioassay results were not available at the time of this report preparation. An updated report will be provided as soon as these results are provided by Dr. Kado.

V. IMPACT OF RESULTS

Funds provided under this grant have further defined the character of snowmobile engine PM emissions. Results complement those produced in an earlier project conducted for the Montana Department of Environmental Quality. This prior work analyzed effects on emissions of different fuels and lubricants, and also provided detailed data regarding emissions of both particulate-bound and vapor phase polycyclic aromatic hydrocarbons (PAHs). These are of concern because this class of hydrocarbons contains several compounds which have been shown to have carcinogenic or mutagenic effects in animal studies.

This work confirmed that two-stroke snowmobile PM emissions are composed primarily of volatile organics, which are principally lubricant derived. Particle diameters were found to be typically less than 100 nanometers, which is of respirable size and able to be delivered into the lung. Results of bioassay analysis of snowmobile PM are pending.

VI. CLOSURE

It has been a pleasure to perform this research for the Yellowstone Park Foundation, Inc. Financial reporting information is included in Appendix E. Please let us know if you have any comments on this study. Southwest Research Institute looks forward to serving any future Foundation research needs.

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and

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APPENDIX A

RESULTS FROM POLARIS ENGINE TESTED WITH POLARIS MINERAL-BASED LUBRICANT AND CONOCO BIO-SYNTHETIC LUBRICANT

APPENDIX B

RESULTS FROM DIRECT FILTER INJECTION - GAS CHROMATOGRAPHY ANALYSIS OF PARTICULATE

APPENDIX C

RESULTS OF PARTICLE SIZING TESTS USING SCANNING MOBILITY PARTICLE SIZER

APPENDIX D

RESULTS OF PARTICULATE BIOASSAY TEST

APPENDIX E

FINANCIAL REPORTING

FIGURE 5. PARTICLE SIZE DISTRIBUTION FOR BASE MODE 1A

FIGURE 6. PARTICLE SIZE DISTRIBUTION FOR BASE MODE 1B

FIGURE 7. PARTICLE SIZE DISTRIBUTION FOR BIO MODE 1A

FIGURE 8. PARTICLE SIZE DISTRIBUTION FOR BIO MODE 1B

FIGURE 9. PARTICLE SIZE DISTRIBUTION FOR BIO MODE 2A

FIGURE 10. PARTICLE SIZE DISTRIBUTION FOR BIO MODE 2B